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ON CHEMICAL SUBJECTS



THE CHEMISTRY OF RUBBER

H. FREUNDLICH



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General Editor : C. S. SALMON, M.Sc.

THE CHEMISTRY OF RUBBER

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THE CHEMISTRY OF RUBBER

BY

H. FREUNDLICH

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WITH 13 DIAGRAMS



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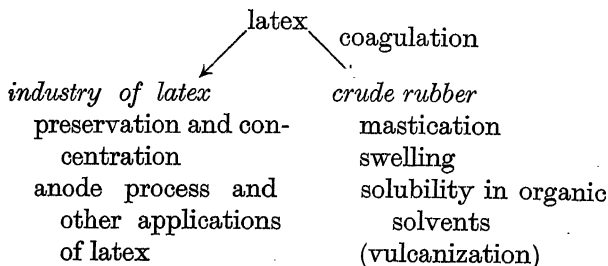
INTRODUCTION

ON one of the first pages of Bancroft's well-known book, *Applied Colloid Chemistry*, the remark is made that colloid chemistry is the physical chemistry of everyday life. To prove this thesis, Bancroft gives a long list of industries and other human activities extending down half a page and commencing with cement, bricks, pottery . . . and ending with . . . photography, illuminants, pharmacology. In many cases only a small number of the processes involved are of colloidal nature, but there are certainly a number of industries, such as tanning, dyeing, &c., which may be described as mainly colloidal. This applies in the highest degree to the industry of rubber, and it is one of the few colloidal industries which has profited decidedly from the modern development of colloid chemistry ; whereas most of the other colloidal industries (tanning, dyeing, &c.) are very old ; in these cases colloid science has on the whole only proved valuable in explaining or improving processes long known.

A short synopsis of the processes involved in the manufacture of rubber articles is meant to

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show the importance of colloid chemistry in this industry.



Rubber is produced from the milky sap or latex of plants specially growing in tropical countries. Latex is like milk or blood, one of those natural colloidal systems, so important and valuable, that industry was forced to overcome the difficulties caused by the intricacies of its composition. In the course of the last twenty years latex has been used more and more for industrial purposes as it is; thus there exists a manifold industry of latex. Till then and also to-day, the greater part of the latex is coagulated very soon after it has left the plant, and the product of coagulation, the crude rubber, is used for manufacturing rubber articles. Crude rubber is easily tacky and markedly plastic, properties not welcome for many practical purposes. Rubber first gained its enormous value when Hayward and Goodyear (in 1838) and Hancock (in 1842) introduced the process of vulcanization: by

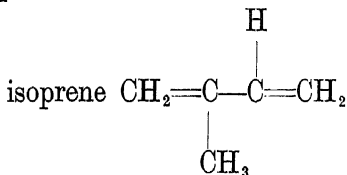
treating crude rubber with sulphur or sulphur-compounds it attains the elasticity so characteristic to rubber and loses its tackiness. In order to be able to incorporate substances like sulphur, then, the co-called accelerators which influence the process of vulcanization in a decisive way, further the fillers, solid powders which are essential for the mechanical properties of the rubber articles, the crude rubber has to be kneaded at a somewhat higher temperature, a process called mastication. Mastication and vulcanization are the two processes specially important when manufacturing rubber articles.

It is obvious from this synopsis, how great a part colloid science plays in the rubber industry : latex and crude rubber are colloidal systems ; colloidal processes are of paramount importance for concentrating and coagulating latex, and practically for all processes making use of latex as it is ; colloidal processes are of great importance in mastication, or when rubber swells in organic solvents or dissolves to a colloidal solution in these solvents. It is only the process of vulcanization which probably cannot be called colloidal ; here purely chemical processes, in the strict sense of the word, seem to prevail.

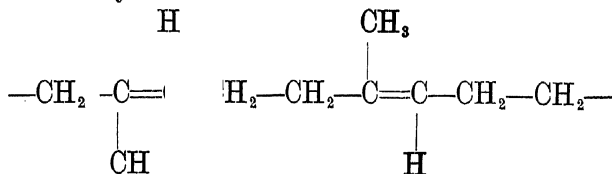
I. LATEX

THE COMPOSITION OF LATEX. THE STRUCTURE OF THE RUBBER PARTICLES IN IT

THE main constituent of rubber is the rubber hydrocarbon produced by the polymerization of isoprene C_5H_8 .



rubber hydrocarbon



Rubber is found in the milky sap of very many plants belonging to quite different genera. Such plants grow also in temperate zones ; the common spurge, belonging to the genus Euphorbiaceae, is a well-known example. Plants of moderate climates have so far not been of technical value. But efforts are made to introduce and to cultivate

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them on a large scale ; experiments of this nature are going on in the U.S.A. with the Guayule-shrub ¹ (*Parthenium argentatum*) and in Russia specially with *Scorzonera tau-saghis*,² both belonging to the genus Compositae.

As yet the monopoly of the latex of tropical plants is unbroken, and although a large number of them might be used, one surpasses all as to importance, owing to the fact that it is grown in large plantations in Malaya : it is the para-rubber tree (*Hevea brasiliensis*) which belongs, like spurge, to the Euphorbiaceae. If latex is mentioned without further comment, it is always the latex of the para-rubber tree which is meant.

In order to obtain latex from the tree, the latter is tapped, the bark being cut in an appropriate way ³ ; the latex exudes slowly at first, then flows out fairly quickly for a certain time, as a white fluid, looking very much like milk. Its concentration as to rubber may vary in a rather broad range, but it amounts generally to 30–35 per cent. Latex contains a large number of other substances which are in part also important for the manufacturing of rubber articles : resins, proteins (1–2 per cent.), sugars and other organic substances such as amines, &c., enzymes, various salts.

The rubber is found in latex in the form of very small particles ; a high percentage of these has colloidal size, below 5000Å, but there is always a good number of larger particles up to 3μ in

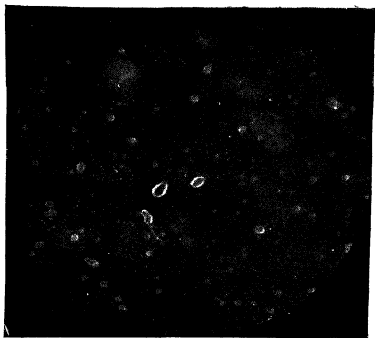


FIG. 1. Microscopic picture of latex of *Hevea brasiliensis*



FIG. 2. Microscopic picture of latex of *Manihot glaciiovii*

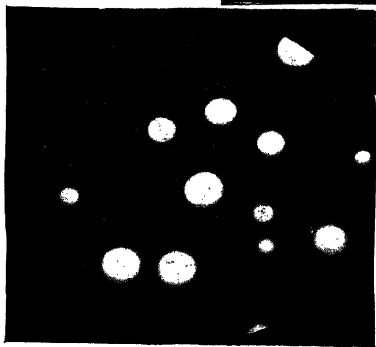


FIG. 3. Microscopic picture of latex of *Ficus elastica*

diameter. The ultramicroscope is therefore not indispensable for seeing the rubber particles as they are in part visible with an ordinary microscope. The number of particles in latex of normal concentration amounts to about $2 \cdot 10^{11}$ per litre.⁴ Thus latex, like milk or blood, is not a colloidal solution of rubber in the strict sense of the word, i.e. one which only contains ultramicroscopic particles. But suspensions with particles up to 10μ do not differ substantially from true colloidal solutions in their whole behaviour.

The particles of the latex of *Hevea brasiliensis* have a rather extraordinary shape; they deviate distinctly more or less from a purely spherical form, and are even to a certain percentage pear-shaped (see Fig. 1), some having quite a long stalk.⁵ This does not only apply to the larger particles directly visible under the microscope; the ultramicroscopic particles are not strictly spherical too, as may be shown by using the cardoid-ultramicroscope with the so-called azimuth-diaphragm.⁶ The particles in the latex of other plants are found to have other shapes; those in the latex of *Manihot glaciarii*—also belonging to the Euphorbiaceae—are rod-shaped (see Fig. 2), whereas those of *Ficus elastica*, a tree of the genus Moraceae, are spherical (see Fig. 3).

These pear-shaped particles of *Hevea*-latex look very much like drops on whose surface solid films have been formed. And this really seems to be

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the case. Their structure may be investigated with a micromanipulator, an apparatus which allows one to operate under the microscope.⁷ This is done with extremely fine needles of glass with tips of a diameter down to $\frac{1}{2}\mu$; one is also able to use hollow needles or micropipettes. They may be moved under the tube of the microscope with the aid of very fine screws. Experiments of this sort showed definitely that the interior of the particles has a honey-like consistence, despite a certain degree of elasticity, whereas the outside layer behaves like a hard and tough skin. Since this skin has practically the same refractive index as the interior, it is generally presumed that it also consists of the rubber hydrocarbon, most likely in a higher polymerized form than that contained in the interior. But it does not seem definitively certain that this skin really is a pure hydrocarbon. Staudinger⁸ favours the assumption that it is a partly oxidized hydrocarbon. Anyhow a purely chemical investigation of the rubber, produced from latex, leads to similar results as was first shown by Caspari⁹: crude rubber may be fractionized into two fractions; the one is fairly easily soluble in organic liquids such as gasolene, ether, &c., the other only swells in them. It is a general experience that solubility goes parallel with the degree of polymerization.

A third factor is further important in the struc-

ture of these particles. They are coated on the outside with an adsorption layer, presumably consisting mainly of proteins and derivatives of proteins (see Fig. 4). This is proved by their electrokinetic behaviour.¹⁰ The particles show pronounced electrophoresis, they migrate under the influence of an electric current to the anode, being negatively charged; this applies

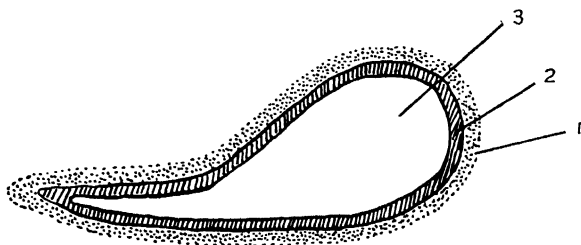


FIG. 4.—Latex particle showing :

1. Adsorption layer.
2. Tough hydrocarbon skin.
3. Viscous hydrocarbon centre.

to the particles in freshly tapped latex whose P_H is about 7·7-2, as well as to latex preserved with ammonia. But it is easy to change the sign of the charge; the particles may be made positive, if we add, stirring strongly, an amount of acid, sufficient to reach a P_H of 3. We pass an isoelectric point having a value of about 4·5-4·8 in the case of fresh latex. Now particles of pure hydrocarbons (paraffin oil, &c.)

never show an isoelectric point, as long as only the P_H is changed ¹¹; with decreasing P_H the electrophoretic velocity simply diminishes and becomes practically zero, as soon as a certain grade of acidity is reached. The existence of a well-defined isoelectric point, depending upon the P_H , is nearly always a sure sign that a surface is covered with a protein. In fluids of natural origin there are very few other substances (cholesterol for instance) which may cause an isoelectric point of this nature.

The coating of the particles with a layer of protein is corroborated by two other facts. The serum of latex—i.e. the aqueous solution remaining after separating off the rubber particles—contains proteins up to 1–2 per cent. It is a general experience that practically all surfaces, whether gaseous, liquid or solid, are immediately covered with a film of protein, when brought into a protein solution ¹²; this has been proved in air bubbles, drops of gasolene, particles of quartz, ZnO, &c. Thus it is also to be expected in rubber particles.

Furthermore, it is generally acknowledged that proteins are mainly responsible for the specific behaviour of different species of plants and animals. If this is true, it might be presumed that the electrophoretic behaviour of the particles of latex, taken from different species of plants belonging to one genus, would be characteristic,

because it would depend upon the specific nature of the protein film. Now this really proves to be true, as was shown by Moyer,¹³ investigating

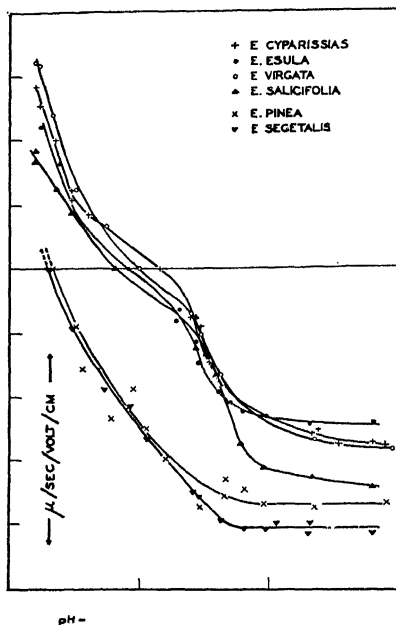


FIG. 5

freshly tapped latex of a great number of species of *Euphorbia* growing in the U.S.A. The curves showing how the electrophoretic velocity depends upon the $\lg P_H$ may be used for determining the taxonomic relationship of these plants. Fig. 5

gives an example of this behaviour ; the species, *Euphorbia segetalis* and *pinea* are closely related, the four other species, *Euphorbia virgata*, *cyparissias*, *esula* and *salicifolia* also form a natural group.

Systems of this kind, where solid or liquid particles are covered with a thin film of protein, are most frequent in nature. If the film is thick enough—a layer of the thickness of one molecule seems to be sufficient ¹⁴—the particles behave like particles of the protein. So far nobody seems to have tested whether the film of protein round the particles of latex is thick enough to make them behave in this way.

ELECTROPHORESIS OF LATEX AND ANODE PROCESS

A technical application of the electrophoresis of latex may be discussed now, although it would be more consistent to treat the preservation and concentration of latex first. As early as 1908 Cockerill ¹⁵ took out a patent for obtaining crude rubber from latex by electrophoresis with movable anodes from which the deposit of rubber was scraped off, as soon as it had attained a certain thickness. This process has not gained ground ; but in the course of the last ten years Sheppard and Eberlin ¹⁶ as well as Klein and Szegvari ¹⁷ have developed a method of manufacturing high-grade rubber articles, wire gauze covered with rubber, &c., using electrophoresis. Many difficulties had

to be overcome. Sulphur, accelerators and fillers have to be added to the latex, and must be deposited together with the particles, in order that the rubber deposit may be vulcanized and have the mechanical properties desired. Yet this does not seem to be so difficult a problem as might be imagined, on account of the fact just mentioned: if all the different kinds of particles in the latex mixture are coated with a layer of protein of sufficient thickness, they all behave like protein particles, migrate with the same velocity, and so may form a deposit having the same composition as the liquid as to solid components. This condition seems to be fulfilled, as far as the publications concerning the process go. The production of gas bubbles on the electrode is another difficulty which had to be overcome. It is rather surprising that quite thick layers of rubber may be produced in this way, although a layer of rubber is such a good insulator. This is explained by the fact that in the fresh deposit the particles have not coalesced, they are separated from each other by thin layers of fluid; the conductivity of the latter accounts for the fact that the deposition goes on after a thin layer of rubber covers the anode. A fresh deposit may be dispersed again by converting the sense of the electric current,¹⁸ a sure sign that the particles as units are still present. They coalesce more and more, as the rubber layer ages.

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If latex, suitably diluted, is electrolysed in a platinum-dish as anode, a small sheet of platinum being cathode, a beautifully coherent skin of rubber is formed in the dish in the course of a minute or so.

PRESERVATION AND CONCENTRATION OF LATEX

Mostly the countries using latex for industrial purposes are in moderate climates ; thus the latex must be transported there from the tropics. This is done in different ways. It may be transported in tank-ships or in drums of different size. Latex is not a stable system ; left to itself the P_H changes from about 7 to about 6.5 in the course of some hours, and this is the cause of coagulation. It may be stabilized by adding a certain amount of ammonia.¹⁹ This is the most popular method of preservation. Formaldehyde and some other substances have also been used successfully.

Since latex contains, as a rule, about 30 per cent of rubber, about 70 per cent of an aqueous solution are shipped without any profit. Thus it was desirable to concentrate latex in such a way that it behaved reversibly, i.e. the fluid regained by diluting concentrated latex must contain the same particles as are dispersed in the original milky sap. Several methods of concentration have been worked out ; a few of the most important ones may be mentioned.

By centrifuging natural latex a stable concen-

trated suspension may be produced containing about 60 per cent of rubber; the Utermark-Latex or Jatex²⁰ is the best-known market product of this kind. Using this method the rubber is separated to a high degree from the non-rubber constituents (proteins, as far as they are not adsorbed on the rubber, &c.) which remain in the serum. Jatex is therefore not a 'whole latex' product containing all of the constituents dissolved in the serum. The importance of this fact may be discussed later. This product of concentration is markedly free of foreign substances; a small amount of NH_3 is added for stabilizing purposes.

A second method, specially developed by I. Traube,²¹ is founded on the fact that the creaming of latex, the accumulation of rubber particles in the upper part of the liquid owing to the difference in density, which proceeds too slowly spontaneously, may be accelerated by adding hydrophilic colloids such as Iceland moss, gum tragacanth, &c. This is most likely a phenomenon of sensitization. These colloids cause a decrease of the ζ -potential of the particles, most likely because they displace some electrolytes on the surface to which the electrical charge is due. This decrease of ζ -potential causes the particles to agglomerate to a certain extent, without making them coalesce. Larger groups of particles formed in this way will cream up more rapidly than the

single particles from which they originated, specially if the temperature is kept about 40–60°. On the other hand, it is quite possible that, on diluting the cream, these groups will be dispersed anew, producing the original particles, since the amount of hydrophilic colloid in the cream is smaller, it having remained to a high percentage in the serum. A certain amount of NH_3 or of another preserving agent has to be added.

As mentioned above, the particles are coated with a film of protein, which may exert a protective action. If the particles in the original latex were protected sufficiently strongly, it might be possible to concentrate latex reversibly, simply by evaporating a certain amount of liquid. Milk may be treated in this way and large amounts of 'dried milk' have been manufactured, a product which dissolves in water to a concentrated emulsion having practically the same properties as milk. A suitable spraying plant is, for instance, constructed as follows ²²: the milk is dropped on a rapidly rotating disk and is thus dispersed into very fine drops which are spread in a large chamber heated from above by a hot blast of air, the powder of dried milk accumulating on the floor of the chamber. If latex is treated in the same way, the sprayed rubber turns out to be very poorly reversible: if one is careful not to compress it in any marked way, it may be dissolved in water or an aqueous solution;

but small pressures are already sufficient to make the product behave irreversibly. Therefore a concentrated reversible latex on a technical scale cannot be made using this method. Nevertheless, 'sprayed rubber' is manufactured to a certain extent in the U.S.A. as a crude rubber.²³ It is a 'whole latex' product containing all substances dissolved in latex, a fact which many consider advantageous. On the other hand, its application is restricted, since it needs high amounts of energy to incorporate fillers, &c.

But another method specially developed by E. A. Hauser turned out to be successful. If suitable, protecting colloids are added to the latex, and if the water is evaporated carefully a reversible concentrated product is produced.²⁴ Soaps are used as protecting agents, and the evaporation is done in a double-walled cylinder heated by hot water. Gelatine, the best-known protecting colloid, cannot be used for this purpose, since its sensitizing action is too pronounced and causes coagulation. This product, called Revertex, may contain 70 per cent and more of rubber. It looks like a thick cream which is easily emulsified by adding water; the emulsion thus formed behaves in most ways like normal latex.

THE LATEX INDUSTRY

Latex, preserved with NH_3 , jatex and revertex, are the products mainly used in the latex indus-

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try.²⁵ This has developed specially on two lines : latex has in part substituted crude rubber ; on the other hand, it turned out to be very valuable for many other industrial purposes owing to its strong adhesive properties.

Latex has supplanted to a great extent solutions of rubber in organic solvents, because the latter have so many disadvantages compared with water as solvent. Rubber articles manufactured by dipping, such as gloves, balloons, &c., are now made very generally by using latex. Sulphur, fillers, &c., are added in a finely powdered form, and many different devices are used for making the layer of rubber sufficiently thick : the viscosity of the dip is increased by adding suitable colloids ; porous moulds are employed through which the serum is sucked, &c. Coagulating dips may be employed, the coagulants, acids or salts, acting upon the layer of latex. From a more theoretical point of view another kind of coagulant dip is interesting, despite the fact that it perhaps has not yet proved to be technically equally advantageous.²⁶ By adding substances such as bentonite, &c., to concentrated latex, the mixture may become thixotropic : when stirred, it is liquid and the mould is dipped in ; the mixture turns solid in course of time, and the mould is pulled out so slowly that it is just covered with a solidified layer. This may be sufficiently thick after one single

dip. Articles made in this way out of latex are dried and vulcanized.

—It is possible to avoid vulcanization as last process : latex may be vulcanized using a method developed by Schidrowitz,²⁷ by adding, for instance, colloidal sulphur, ZnO and a suitable accelerator to the latex. If this product, called vultex, is used instead of latex, the articles need no further vulcanization.—

Similar experimental conditions hold, when substituting latex for solutions of rubber in organic solvents in the processes of spreading and impregnation. The choice of suitable detergents is frequently of great importance. The 'cord' building up the covers of tyres is also impregnated with latex. Cushions of fibres covered with a latex mixture and vulcanized are used for stuffing furniture.

The manufacture of microporous rubber, which presents certain difficulties, when employing crude rubber, turns out to be much easier, when using concentrated latex. The methods differ widely : a foam may be made from the latex mixture as in beating the white of an egg,²⁸ or the mixture is coagulated with suitable electrolytes to a gel which is vulcanized before having lost the water contained in it.²⁹

Rubber threads are made by pressing the latex mixture into a coagulating bath. Only threads with a circular cross-section can be

manufactured in this way, not threads with a square cross-section; the latter must still be made by cutting a thin sheet of rubber. But the threads made from latex are distinctly superior in their mechanical properties, specially in their resistance towards chafing.³⁰

Small articles like balls, toys, &c., are formed in moulds. The liquid latex mixture filling the mould may be solidified by gently heating. The thixotropic mixtures mentioned before can also be used for this kind of manufacture.

The use of latex is found to be not so simple when making tyres, &c., i.e. articles containing very large amounts of fillers of a special kind. It is generally difficult to incorporate them with the latex and this is a drawback for fabrication on a large scale.

Rubber is so generally applied as vulcanized rubber which is not tacky, that one does not always realize that uncured rubber is very plastic and sticky and therefore an excellent adhesive. A fine suspension of rubber in an aqueous solution such as latex is most suitable when making use of these properties of rubber. It is perhaps rather surprising that this side of the latex industry absorbs a high percentage of the raw material.

Latex is one of the best adhesives for leather. It is therefore used on a large scale in the boot-making industry. In the U.S.A. latex has a

similar importance for the canning of preserves. A latex mixture is poured into a groove made by the cover and the box of the tin, and the mass after drying proves an effectual cement.³¹ The great and growing importance of latex in the industry of plastics, of artificial leather, &c., is also, at least in part, due to the extraordinary value of uncured rubber as adhesive.

THE COAGULATION OF LATEX

The greatest part of the latex freshly tapped is coagulated in the tropics to make crude rubber. The latex is gathered in pails and poured into basins lined with tiles. It is diluted to a certain standard concentration by adding water and then coagulated with a suitable electrolyte such as acetic acid or the ammonium salt of fluor-silicic acid.³²

The coagulation of latex is very much like that of an ordinary hydrophobic sol; yet the adsorbed film of protein round the particles makes itself conspicuous in some respects. Since the particles are negatively charged, the influence of the cations prevails according to their valency and adsorbability (see Table 1, p. 18).

The so-called coagulation values given in this table are concentrations of the electrolyte in solution after diluting it with the latex. The latter was fresh and undiluted. The very weak coagulating power of monovalent

TABLE 1³³

Electrolyte	Coagulation values ; millimoles per litre
LiCl	430
KCl	500
Acetic acid	8.5
$(\text{NH}_4)_2\text{SiF}_6$	
2	2.3
MgCl ₂	6
MgSO ₄	16
BaCl ₂ .	12
NiSO ₄	8.0
CuSO ₄	5.8
$\text{Al}_2(\text{SO}_4)_3$	
2	5.0
La(NO ₃) ₃	2.0

cations (K^+ , NH_4^+ &c.) on the one hand, the very strong one of H^+ -ion on the other is not quite the normal behaviour of a negative hydrophobic sol and may be due to the presence of the protein. The influence of the H^+ -ion seems to be overrated sometimes in the literature on coagulation; the polyvalent cations of strong bases such as Ba^{++} , La^{+++} &c., are most active, although their solutions are not hydrolysed and so do not contain a higher concentration of H^+ -ion.

Some investigators³⁴ believe that the coagulation of latex is influenced by the action of an enzyme: fresh latex is said to be markedly stable; first owing to the influence of an enzyme upon the layer of protein round the particles, the stability of the suspension is changed in such a way that it behaves similarly to a hydrophobic

sol. This would mean that latex behaves not unlike the suspensions of some bacilli; they are fairly insensitive towards many electrolytes, until they are transformed into agglutinin bacilli, their surface being changed by the adsorption of agglutinin. According to these investigations, the change of the stability of latex towards electrolytes after heating is also not easily accounted for without assuming the influence of an enzyme.

The coagulation by electrolytes and also the phenomenon of electrodeposition, mentioned above, seem to prove that the latex particles have an extremely pronounced tendency to form large, strongly coherent masses. This fact would be in agreement with a semi-fluid state of the particles.

II. RUBBER

THE STRUCTURE OF CRUDE RUBBER

THE object of coagulation is not only to separate the rubber from the serum, but also to give the product of coagulation, the crude rubber, that structure which is desirable for its future technical application. The fresh coagulate consists of a loose aggregate of particles, separated from each other by thin layers of liquid. This is made most probable by the behaviour, in that very similar experiment, mentioned above, when rubber is electrodeposited: if the sense of the electrical current is reversed, immediately after having deposited a thin layer of rubber, the whole layer can be made to disappear, the particles being dispersed in the liquid. When the film has aged for a short time, this experiment is no longer successful. The coagulated particles approach each other still more, partly coalescing, and this process also depends strongly upon the nature of the coagulating electrolyte and upon many other factors.³⁵ So far no method is known to determine with any degree of certainty how far this process has been going on, or how

many latex particles are still existing in the crude rubber, &c. Therefore the structure of crude rubber is distinctly more problematic than that of latex ; in the latter case the nature of the latex particle, at least, is fairly well understood.

The different forms of crude rubber, crêpe, sheet, &c., depend mainly on the way in which the latex has been coagulated.³⁶ Crêpe is coagulated slowly, the coagulum is soft ; it is milled down, being continuously washed, to thin sheets which are dried in well-ventilated sheds. In order to make smoked sheet, latex is coagulated quickly, in the course of a few hours, the coagulum is passed through rollers and then smoked in a smoke-house ; woods are burnt for this purpose which contain astringent substances in their smoke. The rubber is dried and preserved in this way. The question of preservation is also important, when choosing the coagulating electrolytes.

The method used in manufacturing smoked sheet imitates to a certain extent the old method by which the Indians treated the rubber in the forests of Brazil. They poured the latex tapped from the trees on a stick which was kept rotating in the smoke of a fire ; this was produced by burning a certain kind of nut, the urikuri-nut. The milky sap coagulated on the stick, both the heat and the substances in the smoke being most likely instrumental, forming layer on layer, till at last a fairly large ball of rubber surrounded the stick.

This para-rubber is distinguished from plantation rubber specially by the fact that it contains practically all the constituents dissolved in the latex, whereas, when coagulating the rubber in the way plantation rubber is made, many constituents, such as a high percentage of the proteins, the salts, &c., remain in the serum. Thus para-rubber is a 'whole latex' product; and the same holds for revertex and sprayed rubber, whereas jatex, crêpe and smoked sheet are not 'whole latex' products. This has to be taken into account, when manufacturing rubber articles; the proteins contained in the latex act, for instance, as accelerators, and an article made from a whole latex product is therefore vulcanized quicker, under the same conditions, than one made from a not whole latex product.

As mentioned above, we do not know with any certainty to what degree the particles of latex survive in crude rubber. But we have reason to believe that in any case crude rubber also contains a component which is softer and not so highly polymerized, besides a second component which is harder and more highly polymerized (or oxidized). Experiments by Caspari and others proving this, were discussed above. It cannot as yet be determined in what way these components are distributed and dispersed in another.

But the structure depending upon this factor

Such macromolecules, having not exactly the same degree of polymerization, are lying practically parallel in the crystallite and are joined together by van der Waals' forces. This structure, derived from the X-ray diagram, agrees well with the results derived from investigations on the lines of pure organic chemistry. The crystallites do not make up 100 per cent of the cellulose; a certain amount of non-crystalline foreign substances, water, &c., fill the space between them. Substances such as silk, chitin, &c., have a similar structure.

Chemical changes and other processes may only affect the matter filling the space between the crystallites, leaving the latter unchanged; processes of this kind are called intermicellar. The swelling of cellulose in water and aqueous solutions is an intermicellar process. If the interior of the crystallite is affected by any change, the process is called intramicellar by some investigators; since the terms inter- and intramicellar are easily confounded, it seems preferable to use another word and so the latter kind of changes are often called permutoid processes. It is a true permutoid reaction, when all the macromolecules of cellulose are esterified by HNO_3 to nitrocellulose. The outward look may change very little by such a reaction: normal cotton-wool does not look very different from nitrocotton-wool, though the chemical constitution is strongly

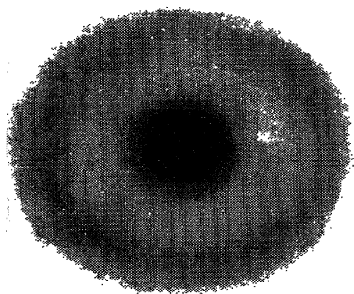


FIG. 6. X-ray diagram of unstretched crude rubber

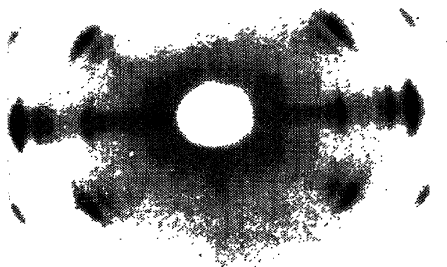


FIG. 7. X-ray diagram of racked rubber

changed. An adsorption is called permutoid if, for instance, a dyestuff enters the crystallite and covers the surface of the macromolecules. A swelling is permutoid if the liquid is taken up by the crystallites and separates the macromolecules from each other. In the case of an intermicellar swelling, such as the one mentioned above, the X-ray spectrum remains unchanged. In the case of a not very radical permutoid swelling, like that of bentonite in water³⁸ or of graphite in sulphuric acid,³⁹ the X-ray diagram is changed in a moderate way, owing to the fact that the macromolecules are now a greater distance from each other. But a permutoid swelling may also cause a radical disorder of the macromolecules, owing to which the crystalline X-ray spectrum is changed to an amorphous one.

The behaviour of rubber is very different from that of cellulose. Whereas fibres of cellulose have the spot diagram caused by oriented crystals, unstretched crude rubber has the X-ray spectrum of an amorphous body (Fig. 6). But as soon as the rubber is stretched to a certain length, a spot diagram appears, as if oriented crystals were formed, a phenomenon first observed by Katz.⁴⁰ As soon as the rubber has returned to its unstretched state, this spot diagram gives place again to the original amorphous diagram. Rubber may be 'racked', i.e. stretched extremely up to 100 times its original length by stretching

it adiabatically and dipping it into hot water ($80-90^{\circ}$) in alternate succession.⁴¹ This racked rubber only shows the spot diagram (Fig. 7), the amorphous one having disappeared entirely. But the position of the spots is independent of the degree of stretching. This fact is strongly in favour of the supposition that the spot diagram is really due to oriented crystals. The following facts point in the same direction: rubber kept for a long time at low temperature, so-called 'frozen' rubber, shows besides the amorphous diagram a Debye-Scherrer diagram, as it is caused by non-oriented crystals (Fig. 8), the circles lying there where the spots appear on stretching (Fig. 9); frozen rubber looks turbid, as if it contained a precipitate of many very small crystals. Specimens of rubber of very different origin all have the same spot diagram on stretching.⁴² Then Hock⁴³ made the following experiment: he cooled strongly stretched rubber down to the temperature of liquid air and hammered it into pieces; these looked like bundles of threads unravelled out at the ends like a fan. Unstretched rubber treated in the same way breaks into irregularly formed pieces like glass.

Although all these facts agree with the assumption that true crystals are formed, there are one or two points which are difficult to understand. The crystals, formed in frozen rubber at low temperatures, remain stable at about room

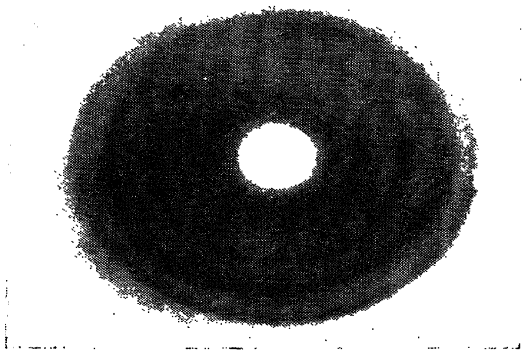


FIG. 8. X-ray diagram of frozen rubber

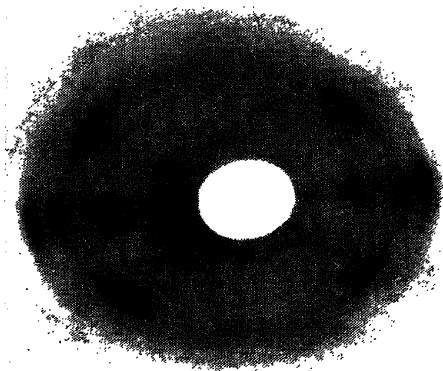


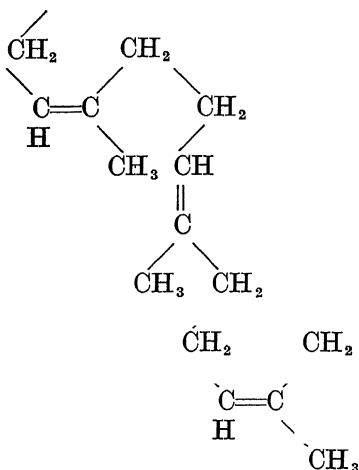
FIG. 9. X-ray diagram of stretched frozen rubber

temperature ; it is therefore hard to explain why the crystals formed on stretching at room temperature disappear when the rubber assumes the unstretched state. This is generally explained by the assumption that the more liquid, less highly polymerized, hydrocarbon in the rubber causes the crystals to swell again in the unstretched rubber ; on stretching the liquid had been pressed out, so to say. In old frozen rubber the crystals, perhaps because they have been formed so very slowly or because of other changes in the rubber due to ageing, must have lost their ability to swell in this way. This explanation is not very convincing, and it is known that some investigators like Wo. Ostwald,⁴⁴ prefer to assume that no true crystals are produced ; he compares the structure of the rubber gel with a kind of network, where by stretching the cords and nodes are brought so near to one another that the orientation of the particles has the same effect as if there were crystals. One would be dealing with a more intermicellar effect. Why this order should be so rigid that the spots in the X-ray diagram of stretched rubber lie exactly there, where the circles of the Debye-Scherrer diagram of frozen rubber lie, and why their position is independent of the degree of stretching, is certainly equally difficult to explain.

Anyhow, the formation of such a crystal-like

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structure by applying a force from outside, favours the supposition that there are smaller units which build up these crystallites. The highly polymerized state of rubber leads again to the assumption that they are macromolecules. Their nature differs in many respects markedly from that of the macromolecules in cellulose. The latter are considered to be straight and rigid ; for the rings of glucose are united by oxygen-bridges, and bridges of this kind are known to be the cause of distinct rigidity : according to W. L. Bragg ⁴⁵ there are oxygen-bridges in the very rigid silicates and Kautsky ⁴⁶ showed that such bridges join together the rigid plate-like macromolecules of very characteristic derivatives of CaSi_2 . Pure rubber, on the other hand, contains no oxygen, and therefore no such bridges ; its macromolecules have no cause to be rigid, it is quite probable that they are flexible and extensible.⁴⁷ Mark and Fikentscher ⁴⁸ have shown that a helical model of a polymerization product of isoprene may be built up in space without difficulty.



Assuming this to be true provisionally it would make the behaviour of rubber quite plausible. Unstretched crude rubber would contain these screw-shaped macromolecules, in different degrees of polymerization, lying entirely at random. Since the X-ray diagram is amorphous, there is no direct cause to assume any micelles or crystallites in the original rubber. The first effect of stretching would be that the macromolecules are oriented more and more; stronger stretching would unscrew and extend them. Where the two CH₂-groups meet, there are, so to say, flexible points; the two groups are capable of being turned, and this would cause the macro-

molecule to be straightened. Such extended molecules lying parallel to each other might unite to form the crystallites shown by the X-ray diagram. The extraordinary elasticity of rubber would be due to this extension of the macromolecules and to the fact that on further stretching the straightened molecules may glide past each other. In racked rubber practically all macromolecules would have united to form crystals. At low temperatures this state may be markedly stable. Owing to the stronger molecular movement the macromolecules would tend to return to their original helical shape at somewhat higher temperature. The crystallites would be destroyed in part, and the amorphous component formed would make them swell; thus the destruction of the crystallites proceeds, until practically the whole mass has returned to the original amorphous state.

The assumption made here, that the stretching of rubber is a rather complex process, is borne out by other facts. Rubber becomes double-refracting,⁴⁹ when stretched, but this effect does not correspond strictly with the appearance of the spots in the X-ray diagram; double-refraction appears already at lower degrees of stretching, and this may be explained by the assumption that the mere orientation of the macromolecules is sufficient to cause it.

This reasoning is hypothetical, as long as the

screw-shape of the macromolecules is not a well-established fact. Other structures of the macromolecule have also been discussed, for instance one which is similar to the structure considered probable for the macromolecule of gelatine: ⁵⁰ in the unstretched state there are, so to say, trunks of crystallites bearing a mass of non-oriented fringes consisting of the long-chain molecules; on stretching the fringes are oriented and form crystallites like the straightened macromolecules, when using the hypothesis of Mark and Fikentscher.

The remarkable structure of rubber is not only shown by its elastic properties and the characteristic features of its X-ray diagram, but also by its caloric behaviour. Whereas most solid substances, metals, &c., become cooler on stretching, rubber becomes warmer, when stretched adiabatically. This phenomenon was already discovered and investigated by Gough ⁵¹ in 1805, rediscovered and reinvestigated by Joule ⁵² in 1859; it is generally known as the Joule effect of rubber. William Thomson (Lord Kelvin) pointed out that, on the ground of thermodynamic reasoning, this anomalous behaviour would lead one to predict that stretched rubber, in contrast to other solids, would contract on heating, extend on cooling, a fact known to Gough and confirmed by Joule. This mechanical effect of heat is so strong that a piece of stretched rubber may be used to trans-

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form heat into mechanical energy. On this principle Wiegand ⁵³ has constructed his rubber pendulum (Fig. 10): the pendulum is adjusted

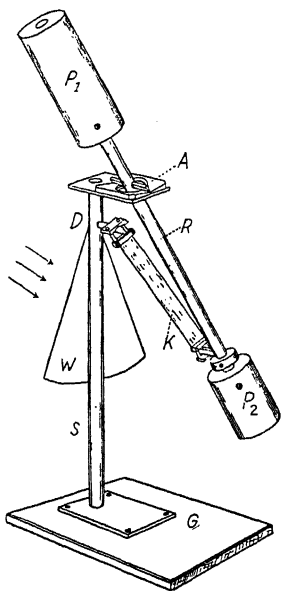


FIG. 10

by two weights, P_1 and P_2 , so that it just swings to the one side; on applying heat by radiation from a lamp—indicated by the arrows—the piece of rubber K contracts and pulls the pendulum toward the other side. Thus it is brought into

a cooler region protected from the radiation of the lamp by the screen W ; this causes a lowering of the temperature of the rubber, a cold blast of air augmenting this effect. On cooling, the rubber extends anew, and the pendulum is inclined fully to the other side. There it is heated afresh by the radiation of the lamp and thus is moved again to the other side.

The Joule effect has not been explained with full certainty.⁵⁴ It does not seem to be due to some kind of intermicellar effect caused by a kind of network of latex particles surviving in the crude rubber, as was assumed by some investigators ; they considered the heat evolved to be a heat of compression, the more liquid phase in the interior of the particles being compressed by the surrounding layers of more highly polymerized tougher rubber hydrocarbon. It is more probable that the main factor is a heat of crystallization produced, when the crystallites are formed out of the macromolecules. A closer investigation has revealed the importance of other factors too : a heat effect due to a change of volume of the macromolecules and one due to friction, when they glide past each other. Thus this caloric effect does not allow any straightforward thermodynamic reasoning.

This discussion is an example of the difficulties met with, when trying to explain phenomena observed in crude rubber. One may have to

choose between an intermicellar effect or one due to the macromolecules, or may have to decide how far both may come into play.

How strongly a difference in mechanical properties is reflected by a difference in the behaviour of the X-ray diagram, is shown by a comparison of rubber with gutta-percha. The difference is due to the hydrocarbons, not to the presence of different kinds of impurities.⁵⁵ Gutta-percha does not show the strong elasticity of rubber; it is tough at lower temperatures and turns soft and plastic on heating. On investigating the X-ray spectrum at different temperatures,⁵⁶ it was found that there is a point of transition at 68°. At temperatures below this point a Debye-Scherrer diagram is observed; it is due to two different forms of gutta-percha crystals which represent two states, correlated to each other by a monotropic change. Above 68° the diagram becomes amorphous. Thus gutta-percha is plastic when the X-ray diagram is amorphous, but it is hard and tough when its state is microcrystalline.

THE MASTICATION OF RUBBER

As mentioned above, mastication and vulcanization are the two processes most important, when treating crude rubber. It must be masticated, else one is not able to incorporate the solid substances, which are necessary for vulcanization and for producing the mechanical properties

wished for. Rubber is masticated by milling it between two cylinders heated to a somewhat higher temperature and rotating in opposite directions at different speeds.⁵⁷ In this way strong shearing forces are exerted upon the rubber. It becomes much softer and more plastic. Mastication is explained in different ways. Some assume that the distribution of the two components in it, of soft, not highly polymerized rubber and of tough highly polymerized, is changed, the soft, plastic rubber becoming the continuous phase, owing to a destruction of the latex particles surviving in the crude rubber.⁵⁸ Others prefer the supposition that the macromolecules are cracked in part, the masticated rubber therefore consisting of less highly polymerized molecules.⁵⁹ Probably both factors have to be taken into account. The conditions prevailing during mastication are further so, that there is every likelihood of oxidation,⁶⁰ a factor always of importance, when dealing with rubber, but not easy to eliminate or to determine quantitatively.

The change caused by mastication is strong, perhaps stronger than might be expected. The rubber becomes extremely plastic when overmasticated, and it turns out to be impossible to use it for making rubber articles of normal elastic and mechanical properties after being vulcanized. For technical purposes rubber must therefore be masticated with great care, in order that it does

not lose its 'nerve'. This change is not absolutely irreversible; in course of time very strongly masticated, highly plastic rubber regains some of its original elastic strength. This is a phenomenon similar to those called thixotropic; ⁶¹ perhaps not in so far that a sol is transformed to a gel, but it is more like the phenomenon that a concentrated sol, originally highly viscous, yet reduced to lower viscosity by shaking or stirring, turns strongly viscous again, when left to itself.

THE SWELLING AND SOLUBILITY OF RUBBER IN ORGANIC LIQUIDS

The change caused in the rubber by mastication is also shown by a strong difference in the behaviour of non-masticated and masticated rubber towards organic liquids such as gasolene, benzene, carbon disulphide, &c. Strongly masticated rubber is dissolved in them forming colloidal solutions, whereas unmasticated rubber swells in these liquids, setting aside the generally only small amount which is dissolved. The phenomenon of swelling and the behaviour of rubber in colloidal solution seem to be nearly related and they are interesting specially from a theoretical and less from a technical point of view.

Swelling is characterized by the swelling pressure which may be determined with the following apparatus ⁶² (Fig. 11): a disk of rubber is put at the end of a glass tube on the wall of

a porous cell which is cemented to the tube. The whole is dipped into a beaker containing the organic liquid. The tube is filled up with mercury, which partly also fills the capillary. The end of the capillary is joined to a bomb containing compressed air; thus well-defined pressures may be applied, and the change of volume of the

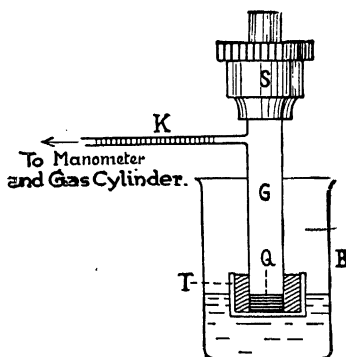


FIG. 11

rubber disk may be calculated from the position of the mercury in the capillary. Since the porous cell is impermeable to dissolved rubber, a certain tendency to dissolve does not cause any disturbance.

Well-defined values of equilibrium are obtained in this way and the swelling pressure π may be correlated to the concentration of the rubber in

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the swollen rubber-gel γ (in grams per 1000 c.c.) by a formula

$$\pi = \pi_0 \gamma^n \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where π_0 and n are constants. Logarithmizing

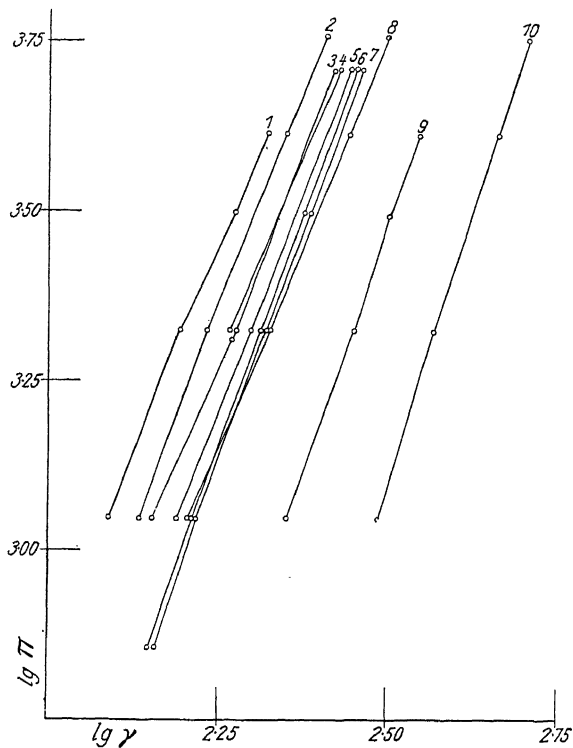


FIG. 12

this formula a linear relation is obtained. The logarithmical diagram (Fig. 12) with $lg \pi$ and $lg \gamma$ as co-ordinates, proves the correctness of formula 1, and further the fact that n varies very little with the nature of the organic liquid; the lines are practically parallel, the values for n lie between 2.5 and 3.3.—The lines in Fig. 12 correspond to the following liquids: 1, carbon tetrachloride; 2, chloroform; 3, acetylene dichloride; 4, tetrachloroethane; 5, toluene; 6, thiophene; 7, benzene; 8, cymene; 9, ether; 10, ethylene dichloride.—

The swelling of rubber is one of the not very frequent cases where thermodynamic reasoning has been applied successfully to colloidal phenomena. By an isothermal process the swelling pressure may be correlated to the vapour pressure p of a swollen rubber-gel by the formula ⁶³

$$\pi = \frac{RT}{M_0 V_0} \ln \frac{p}{p_s} \quad . \quad . \quad (2)$$

Here V_0 is the specific volume of the liquid, M_0 its molecular weight, p_s is the saturation pressure of the liquid for the given temperature, R and T are the well-known terms. Experiments by Stamberger ⁶⁴ (Fig. 13) show a fairly good agreement between the values of π calculated according to formula 2 and those measured directly. The curve on the right refers to C_6H_6 , that on the left to CCl_3H .

The properties of the colloidal solutions of rubber which have been specially investigated are their osmotic pressure and their viscosity. The osmotic pressure of rubber solutions in organic liquids (gasolene or benzene) may be determined directly by using skins of vulcanized rubber,

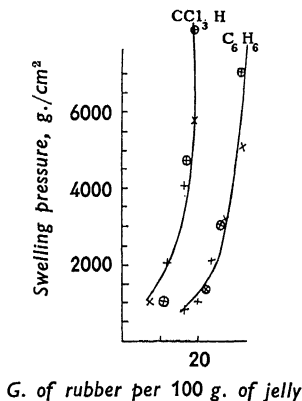


FIG. 13

⊗ Calculated.

× Posnjak's measurements,

which are insoluble in these liquids, as semi-permeable membranes.⁶⁵ In some respects these solutions represent systems of a very simple kind: particles of a poorly soluble hydrocarbon in a hydrocarbon medium; all the complications found in colloidal aqueous solutions (of carbohydrates, proteins, &c.), caused by their being solutions of colloidal electrolytes and their giving

rise to Donnan equilibria, &c., may be neglected in these rubber solutions.

Nevertheless, the simple equation of van't Hoff

$$PV = RT$$

does not hold. According to G. V. Schulz,⁶⁶ the results may be represented by a formula similar to the simplified equation of van der Waals

$$P(V - b) = RT,$$

if b is considered to be variable and proportional to the amount of solvent bound to the particles of rubber. Schulz uses an equation

$$P(V - \alpha gs) = \frac{g}{M_R} RT \quad . \quad . \quad (3)$$

Here g is the amount of solute dissolved in V c.c., s the volume of 1 gramme of solute plus the volume of bound solvent, M_R is the molecular weight of the rubber in solution, α is a constant. M_R is assumed to be practically constant, the molecular weight not considered to deviate strongly from an average value.

In attempting to correlate the swelling pressure quantitatively with the osmotic pressure of rubber solutions Schulz makes the supposition that the forces, binding the molecules of the solvent to the rubber particles in solution, are identical with those which cause the rubber gel to swell. He assumes, further, that in the case of equilibrium this 'pressure of solvation' π_s is equal to the

osmotic pressure P : the forces in the solution, acting in such a sense that they deprive the rubber particles of molecules of solvent, are considered to be identical with the forces acting upon the free solvent across a semipermeable membrane. This taken for granted, π_s and therefore P ought to depend upon s in the same way as the swelling pressure π would depend upon s , if this quantity were introduced into equation (1), instead of γ . The latter equation would then be transformed to

$$\pi = ks^{-n} (4)$$

This equation was found to hold, indeed, if the values for $\pi_s = P$ and s were introduced; n had the right value too, lying between 2.4 and 2.7.

Even an agreement in the absolute values may be made probable on the ground of the data determined so far. Equation 3 allows one to calculate $\alpha.s$ and not s . But it is not improbable that α does not differ much from unity. Making this assumption s may be extrapolated according to equation 4 for values of π equal to such values of P as were determined experimentally, and be compared with values of s derived from osmotic measurements. Table 2 (opposite page) shows that these values agree very satisfactorily.

These reflections are all the more probable, since in the case of rubber the transition of sol to gel and vice versa is most continuous and gradual. It fits in, further, with the fact that

TABLE 2

RUBBER IN BENZENE

P (in atmospheres)	s (litres per gram of rubber)	
	Calculated from osmotic measurements (Caspari ⁶⁵)	Extrapolated from determinations of swelling pressure (Posnjak ⁶²)
0.012	0.031 ₅	0.024
0.059	0.016	0.016 ₅

the swelling of rubber in organic solvents is permutoid: the spot diagram of stretched rubber disappears when the rubber swells in an organic liquid.⁶⁷

The viscosity of rubber solutions has been investigated still more frequently and has been used extensively for theoretical deductions. At higher concentrations of rubber, Newton's law and hence also Poiseuille law do not hold,⁶⁸ as is often the case in concentrated colloidal solutions; this is most likely due to an internal structure. Only for weak concentrations, if at all, a normal coefficient of viscosity may be determined. The equation of Einstein referring to the viscosity coefficient of suspensions containing not too small, rigid, spherical particles,

$$\eta_{\phi} = \eta_{\mu}(1 + 2, 5\phi)$$

also does not hold.⁶⁹— η_μ and η_ϕ are the coefficients of viscosity of the medium of dispersion and of the sol, ϕ is the volume of the suspended particles per unit volume of the suspension.—Staudinger⁷⁰ correlates viscosity and concentration of the sol c by an equation

$$\lg \frac{\eta_\phi}{\eta_\mu} = K_c c \quad (5)$$

and claims the constant K_c to be very generally proportional to the molecular weight M of the colloidal substance in solution

$$M = K_m \cdot K_c \quad . \quad . \quad . \quad . \quad (6)$$

He has tested these deductions upon a large series of more or less highly polymerized, synthetic organic substances (polyoxymethylenes, polystyrols, &c.). It is probable that Staudinger is right for the cases of colloids having not too high a molecular weight, so-called hemicolloids (up to about 50,000). Whether these reflections may be extended to solutions containing larger particles, is perhaps open to discussion. Calculating the molecular weight of rubber in solutions of benzene, &c., in this way values up to 150,000 are found.

Staudinger⁷¹ suggests that this proportionality between the constant K_c and the molecular weight may be explained by assuming rod-shaped, rigid particles which are not solvated. But according to Werner Kuhn,⁷² such a constitution of rubber

solutions would involve a quite different relationship between the constant K_c and molecular weight, not a simple proportionality. He proposes a tangle of filiform, flexible particles and an influence of solvation. The latter seems indispensable, if only because it is difficult to explain in another way the swelling of rubber and its correlation with the behaviour of rubber solutions. It is probable that a future successful theory of these phenomena will allow one to calculate the degree of solvation from data derived from swelling on the one hand, from osmotic pressure and viscosity on the other.⁷³

FILLERS IN RUBBER

Crude rubber has to be masticated, in order to introduce solid or liquid substances such as sulphur, accelerators, fillers, oils which are needed for vulcanization and for giving the rubber the mechanical properties wished for. The influence of fillers is specially interesting from a colloidal point of view. The mechanical properties of the final rubber product, its toughness, resistance, &c., depend strongly upon the nature of the fillers used. Thus the very great tensile strength of the rubber used for tyres is attained by adding large amounts of carbon in a highly dispersed state, not every carbon being equally good, carbon black manufactured in a special way by incomplete combustion of natural gas, for instance,

is most efficient.⁷⁴ Mixtures of a plastic mass and finely dispersed solids excel frequently as to their mechanical properties. Portland cement and concrete are further examples of this fact. It is essential for all systems of this kind that they contain a very great number of solid particles, involving a very large area of solid surface, and that these particles are cemented to each other by very thin layers of a plastic mass, becoming harder in the course of time or under a certain treatment. In the case of Portland cement the cement uniting the particles is produced by the interaction of the particles with water. In the case of rubber articles the crude rubber represents the plastic cement, the large surface of solid particles being produced by incorporating the filler. Owing to the difference in the area of this surface and specially in the forces of attraction between the solid particles and the plastic mass, different kinds of powders produce masses having very different mechanical properties. It was shown that under similar conditions a higher degree of dispersion of the filler favours a higher tensile strength of the rubber product.⁷⁵ Comparing fillers of a similar kind there is a parallelism between their favourable influence upon the mechanical properties and their capacity of adsorbing substances such as acetic acid or dyestuffs in an aqueous solution ; ⁷⁶ from this fact one may deduce that the

surface affinity of the solid powder towards organic substances is of great importance. The following experiments by Stamberger⁷⁷ are perhaps still more conclusive in this respect. He dissolved strongly masticated, unvulcanized rubber containing a certain amount of filler in gasoline and covered this suspension with pure gasoline. The rubber spreads into the pure liquid transporting the powder to a certain extent, a phenomenon looking like a case of diffusion, but being most likely caused by a process of swelling. There is a parallelism (cf. Table 3) between the amount transported and the reinforcing strength of the filler, as is shown, for instance, by the great difference between carbon black and BaSO_4 . This behaviour is easily understood. The organic solvent displaces to a certain degree the rubber from the surface of the filler. The greater the affinity between filler and rubber, the larger is the amount of filler remaining bound to the rubber.

TABLE 3
RUBBER PLUS FILLERS IN BENZENE

Filler	Amount transported
Barytes	0.37
Clay . . .	2.0
MgO . . .	44.0
Lead oxide	44.1
MgCO ₃ . . .	87.5
ZnO . . .	98.0
Gas black .	100

A very active kind of carbon black solidified the whole mass to a gel, as if the tensile strength of the rubber, so strongly reduced by mastication, had been restored by this most active filler.

VULCANIZATION AND OXIDATION OF RUBBER

The process of vulcanization is of paramount importance : the crude rubber loses the tackiness which manifests itself at higher temperatures ; it becomes, further, more elastic and less plastic, not showing any permanent extension even when stretched very strongly. Vulcanization may be obtained in different ways. The most usual method is to vulcanize at higher temperatures : the mixture of rubber, sulphur (up to 8 per cent), accelerators (and fillers) is heated to about 140° in over-heated steam. Rubber mixtures depending upon the nature and amount of accelerator may also be vulcanized at low temperatures, by simply dipping them for a short time into a solution of S_2Cl_2 in CS_2 or similar organic solvents.

Although an enormous amount of experimental work has been done to explain the phenomenon of vulcanization, it is rather disappointing to see how little is really known. Colloidal processes do not seem to come in to any marked extent, despite the decided preference of some investigators.⁷⁸ Purely chemical changes are most likely mainly important ; but it is not easy to account for the mechanism of the reactions going

on. This is partly due to the fact that they proceed in the interior of a gel, and that a change in the mechanical properties is practically the only indicator revealing that the reaction has taken place. It is a well-established fact that the rubber hydrocarbon is able to react with sulphur: ebonite, the rubber product made by heating rubber with a larger amount of sulphur (40 per cent and more) for a longer time, is a compound $(C_5H^8S)_n$. But it is not obvious what happens under the much milder conditions prevailing when vulcanization goes on. Meyer and Mark ⁷⁹ assume that sulphur-bridges between the double-bonds of neighbouring macromolecules may unite groups of them to larger complexes. These bridges might prevent the macromolecules from gliding along each other, i.e. they would reduce the plasticity of the rubber; the strong elasticity, still remaining, would be due to the extension of the screw-shaped macromolecules. Boggs and Blake ⁸⁰ assume that only the double-bonds of the end-groups of each single macromolecule react with sulphur. If this is so, then vulcanization would be another characteristic case of the strong change in chemical and mechanical behaviour caused by a reaction of end-groups, a phenomenon specially discussed by Staudinger ⁸¹ for the macromolecules of polyoxymethylenes.

The following facts agree with the assumption of a chemical reaction or with the more special

supposition of bridges between macromolecules. A similar, but reversible change of elastic and plastic properties, as is caused by vulcanization, may also be produced by cooling rubber to suitably low temperatures⁸² (-50°). Probably the higher viscosity is disadvantageous to gliding and therefore reduces the plasticity. Other substances which are apt to form bridges between the macromolecules (selenium, tellurium, benzoylperoxide, aromatic nitrocompounds) seem to react with rubber in a similar way to sulphur; a kind of vulcanized product is formed.⁸³ Sulphur, on the other hand, is able to react with other organic macromolecules containing double-bonds, for instance those of linseed oil, generating solid, elastic products of 'vulcanization', the so-called factice.⁸⁴

Schidrowitz⁸⁵ has shown, as mentioned above, that it is possible to vulcanize the rubber particles in latex by treating them, for instance, with colloidal sulphur, ZnO, suitable organic accelerators at not so very high temperatures. This process may be investigated by testing the behaviour of the particles under the microscope with the needle of a micromanipulator, as was described above. The changes found seem to prove definitively that vulcanization is chiefly a chemical process.⁸⁶ In the first stages of vulcanization the viscosity of the particle decreases; it is most likely owing to this that the

particles lose their pear-like shape and become spherical, the surface-tension being able to prevail. In later stages the particles grow more and more tough, as if the formation of a gel was taking place; this process goes on fairly slowly from without to within. Thus the particles of vulcanized latex are hard and elastic like little rubber balls, and therefore markedly distinguished from the more plastic particles of natural latex. The changes observed are subtle and intricate, and it seems improbable that they should be due to a simple and straightforward process such as adsorption, for instance, and not to a more complicated process such as a chemical reaction.

Though it perhaps may be taken for granted that vulcanization is mainly due to a chemical change, there are many points in its mechanism which are hard to understand, for instance the action of accelerators, inorganic ones like MgO , PbO , &c., and the large number of organic ones; they are basic nitrogen compounds, organic substances containing the $-\text{S}-\text{H}-$ group and xanthates. These accelerators are not characterized fully, if they are only designated as catalyzers. They do not merely accelerate a reaction, which would go on in exactly the same way in their absence, but the amounts of the reacting substances seem to be influenced too: in presence of some very efficient accelerators a much smaller

percentage of sulphur—down to 1 per cent—may be applied. Some accelerators or some combinations of accelerators may be used even without adding any sulphur. This fact, and perhaps also some others, are in favour of the assumption that it is mainly the reactivity of the sulphur which is changed by the accelerator. It is well known that the rate at which the manifold isomeric and polymeric molecules of sulphur are formed depends strongly on the catalytic action of foreign substances, a phenomenon which also lacks a plausible explanation. The possibility that a special form of sulphur is instrumental in causing vulcanization is plausible and has been discussed,⁸⁷ but has not resulted in any general theory.

It was mentioned more than once that rubber is most easily oxidized, a fact which is technically important in many ways. The colloidal properties of rubber manifest themselves here even less than in the case of vulcanization ; this whole question need therefore not be discussed extensively. It may be remarked that the phenomena correlated with the oxidation of rubber are distinctly similar to those found, when oxidizing other organic compounds containing many double-bonds, for instance linseed-oil.⁸⁸ Metals such as copper, manganese, &c., are powerful positive catalyzers ; organic substances, known as anti-oxidants such as hydrochinon, &c., are also active

in the case of rubber. The oxidation of rubber is further catalyzed by light, specially ultra-violet light.⁸⁹ These rays also seem to be able to cause a depolymerization of rubber.

III. SOME REMARKS ON THE BOTANY OF LATEX-PRODUCING PLANTS AND ON THE HISTORY OF THE RUBBER INDUSTRY

THE STRUCTURE OF THE LATEX PARTICLE FROM A BOTANICAL POINT OF VIEW

THE botanical questions raised by growing large plantations of *Hevea* trees have been thoroughly investigated.⁹⁰ Some are closely correlated to colloidal problems, and most of these are not easy to explain. It was mentioned above how strongly the structure of the particles differs, when different kinds of latex-producing trees are compared: the particles in the latex of *Ficus elastica* are spherical and distinctly liquid; those of *Manihot glaciarii* rod-shaped and solid; those of *Hevea brasiliensis* pear-shaped and having that rather complicated constitution discussed already extensively. According to Hauser,⁹¹ even specimens of *Hevea* trees may be distinguished from each other by the shape of their particles; subtleties in the shape, specially in the 'stalks' of the 'pears' are said to be characteristic and to allow one to tell, by

looking into the microscope, from which individual tree the latex was tapped. The age of the tree manifests itself in the size and shape of the particles⁹²; the latex coming from different parts of the plant (roots, stem, leaves, seeds, &c.) may also be distinguished in this respect.

The extraordinary shape of these particles does not seem to be due to their being formed by some special mechanical device: one might believe they had been pressed out of an orifice. They are said to have been formed in the interior of the sap. Thus one is dealing again with the problem frequently met with in colloid science and not easily answered: why are non-spherical particles produced, even when they are not distinctly crystalline, and why are in the case of crystals belonging to the regular system non-isometric particles formed, plates or rods, instead of cubes, octahedra, &c.?

A more thorough investigation of latex and rubber from different kinds of latex-producing plants would also be of interest. It was mentioned above that the particles of *Hevea brasiliensis* were very different from those of *Manihot glaciivii* or of *Ficus elastica*; on the other hand, that crude rubber from very various sources gives the same X-ray diagram. Such investigations might make it easier to decide the question, how far the structure of the particles is responsible for the behaviour of the crude rubber.

SOME HISTORICAL REMARKS

The history of the rubber industry is interesting and deserves to be given in a short summary.⁹³

When America was discovered by the Spaniards, they found the natives using primitive rubber articles, balls, shoes, &c. The natives even seem to have succeeded in vulcanizing them, by adding occasionally sulphur or gunpowder to the latex.⁹⁴ But somewhat larger amounts of rubber did not come over to Europe before the second half of the eighteenth century. From that time on a rubber industry may be said to exist. The English term for this substance is derived from one of the first ways of using it, namely to eradicate pencil-marks; rubber was introduced for this purpose by Priestley in 1770. Already in 1780 rubber tubing was employed in scientific experiments by Ingen-Housz in Holland. In 1823 Macintosh took out a patent for impregnating cloth with rubber solutions and thus for manufacturing those weather-proof fabrics known under his name. It was a serious drawback that the rubber was not vulcanized; the weather-proof cloths became sticky in warm weather, hard in cold. Vulcanization was introduced by Hayward and Goodyear in the United States (1838) and Hancock in England (1842). Lüdersdorff in Germany had noticed already in 1832 that rubber lost its tackiness on adding sulphur,

but did not make use of this fact for technical purposes. Thanks to the invention of vulcanization the main difficulty in the manufacturing of rubber articles was overcome, and the use of rubber grew steadily and strongly since then.

In the course of time it became evident that supply and demand were not satisfactorily balanced. Rubber was only obtained by tapping latex-giving trees growing wild in the tropical forests, specially in Brazil; its properties were varying, latex was no marketable product. Obviously it would have meant a great improvement if rubber could have been made a product obtained in a regular way from large plantations. The Marquis of Salisbury, then Secretary of State for India, Sir Clements Markham, Sir Joseph Hooker, the celebrated botanist, were among those men who were interested in the plan for introducing rubber plantations to India and Malaya. Experiments done with different trees, producing latex, led to the result that the *para*-rubber tree, *Hevea brasiliensis*, growing in the forests of the Amazon River, had the best prospects. Mr. Henry Wickham, in later years Sir Henry, who had plantations in Santarem on the Amazon, succeeded in gathering large amounts of seeds of the Hevea tree. Without waiting for an official order from the Indian Government he chartered a steamer lying without return-cargo on the river, and smuggled the seeds, about

70,000, out of Brazil; they arrived safely in Liverpool in June 1876. They were sown in Kew Gardens, but only about 4 per cent grew up to plants. A few years later these plants were distributed to different places of Ceylon, the Straits Settlements, Java, and all the large plantations existing there have sprung from these seeds.

At the end of last century plantation rubber appeared on the market. At the beginning of the new century the demand for rubber grew enormously, owing to the use of tyres in the motor-car industry. In those years the competition of the plantation rubber was not strong enough to prevent an enormous rise in the price of rubber. There was a 'boom' in 1910, the price of rubber amounting to about 13s. a pound. In that year about 94,000 tons of rubber were imported; 88 per cent were wild rubber, 12 per cent plantation rubber. But the competition was soon decided in favour of the plantation rubber: in 1933 from about 800,000 tons of rubber only 1.5 per cent were wild rubber; the price of the pound was about 6d.

Latex, which had been a rarity as long as wild rubber ruled the market, soon became a well-known product, and specially in the course of the last fifteen years that industry of latex has developed which I have often referred to. The beginning of this century also saw the prosperous

development of colloid science. It was therefore no wonder that this newly gained knowledge was applied in solving problems brought forward by the young industry of latex. Here we have one of the first cases, where colloid chemistry has proved itself to be a physical chemistry of everyday life on a really large scale.

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